

REMARKS

This is in response to the Office Action that was mailed on April 17, 2006. The definition of R^3 in claim 1 has been amended, based upon the working Examples. Clerical errors related to the terms $T\alpha\beta$ and $T\alpha\beta$ have been corrected in the specification and claims. That the correction is proper is manifest on the face thereof, and is supported by publications available to persons skilled in the art, including EP 0718325 A (page 6, line 55 through page 7, line 40) and EP 0751182 A (page 8, line 33 through page 9, line 16). Copies of these publications are enclosed for the convenience of the Examiner. The feature of claim 2 has been incorporated into independent claim 1. No new matter has been introduced. Claims 1 and 3-27 are pending in the application, with claims 10-27 being withdrawn from consideration on their merits.

Claims 1-9 were rejected under 35 USC § 102(b) as being anticipated by an article authored by Aaltonen et al. The rejection is respectfully traversed. The Aaltonen et al. article discloses a copolymer of ethylene and propylene with 10-undecen-1-ol, having a molecular weight distribution (M_w/M_n) of not more than 3, prepared in the presence of various metallocene catalysts. However, the Aaltonen et al. article does not teach a polar-group-containing olefin copolymer as defined in present claims 1, 6, and 9.

As discussed in the specification, page 3, line 13 through page 4, line 6, copolymers prepared by copolymerizing α -olefins with polar group-containing monomers using a Ti catalyst (Ziegler-Natta catalyst) or V catalyst have a non-uniform molecular structure. That is, these known copolymers have, e.g. a wide molecular weight distribution or high inversion content.


The polar group-containing olefin copolymer of the present invention solves the above-described problem on non-uniform molecular weight. Moreover, it has a satisfactory orientation of polar groups towards the interface between the copolymer and polar materials, as well as sufficient adhesion properties to polar materials and compatibility therewith. The Aaltonen et al. article neither teaches nor suggest the above. No person of ordinary skill in the art would conceive of these superior effects of the present invention based upon the Aaltonen et al. disclosure.

Accordingly, the presently claimed invention is both novel and unobvious. The Examiner is earnestly requested to withdraw the rejection under 35 USC § 102(b), and to pass this application to Issue.

Should there be any outstanding matters that need to be resolved in the present application, the Examiner is respectfully requested to contact Richard Gallagher (Reg. No. 28,781) at the telephone number of the undersigned below, to conduct an interview in an effort to expedite prosecution in connection with the present application.

Respectfully submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

By 

Marc S. Weiner, #32,181

MSW/RG
1155-0274P

P.O. Box 747
Falls Church, VA 22040-0747
(703) 205-8000

EP 0 718 325 A2

3-methyl-1,4-hexadiene, 4-methyl-1,4-hexadiene, 5-methyl-1,4-hexadiene, 4-ethyl-1,4-hexadiene, 3-methyl-1,5-hexadiene, 3,3-dimethyl-1,4-hexadiene, 3,4-dimethyl-1,5-hexadiene, 5-methyl-1,4-heptadiene, 5-ethyl-1,4-heptadiene, 5-methyl-1,5-heptadiene, 6-methyl-1,5-heptadiene, 5-ethyl-1,5-heptadiene, 3-methyl-1,6-heptadiene, 4-methyl-1,6-heptadiene, 4,4-dimethyl-1,6-heptadiene, 4-ethyl-1,6-heptadiene,

4-methyl-1,4-octadiene, 5-methyl-1,4-octadiene, 4-ethyl-1,4-octadiene, 5-ethyl-1,4-octadiene, 5-methyl-1,5-octadiene, 6-methyl-1,5-octadiene, 5-ethyl-1,5-octadiene, 6-ethyl-1,5-octadiene, 6-methyl-1,6-octadiene, 7-methyl-1,6-octadiene, 6-ethyl-1,6-octadiene, 6-propyl-1,6-octadiene, 6-butyl-1,6-octadiene,

4-methyl-1,4-nonadiene, 5-methyl-1,4-nonadiene, 4-ethyl-1,4-nonadiene, 5-ethyl-1,4-nonadiene, 5-methyl-1,5-nonadiene, 6-methyl-1,5-nonadiene, 5-ethyl-1,5-nonadiene, 6-ethyl-1,5-nonadiene, 6-methyl-1,6-nonadiene, 7-methyl-1,6-nonadiene, 6-ethyl-1,6-nonadiene, 7-ethyl-1,6-nonadiene, 7-methyl-1,7-nonadiene, 8-methyl-1,7-nonadiene, 7-ethyl-1,7-nonadiene,

5-methyl-1,4-decadiene, 5-ethyl-1,4-decadiene, 5-methyl-1,5-decadiene, 6-methyl-1,5-decadiene, 5-ethyl-1,5-decadiene, 6-ethyl-1,5-decadiene, 6-methyl-1,6-decadiene, 6-ethyl-1,6-decadiene, 7-methyl-1,6-decadiene, 7-ethyl-1,6-decadiene, 7-methyl-1,7-decadiene, 8-methyl-1,7-decadiene, 7-ethyl-1,7-decadiene, 8-ethyl-1,7-decadiene, 8-methyl-1,8-decadiene, 9-methyl-1,8-decadiene, 8-ethyl-1,8-decadiene,

6-methyl-1,6-undecadiene and 9-methyl-1,8-undecadiene;

alicyclic polyenes, such as

vinylcyclohexene, vinylnorbornene, 5-ethylidene-2-norbornene, dicyclopentadiene, cyclooctadiene, 2,5-norbornadiene,

1,4-divinylcyclohexane, 1,3-divinylcyclohexane, 1,3-divinylcyclopentane, 1,5-divinylcyclooctane, 1-allyl-4-vinylcyclohexane, 1,4-diallylcyclohexane, 1-allyl-5-vinylcyclooctane, 1,5-diallylcyclooctane, 1-allyl-4-isopropenylcyclohexane, 1-isopropenyl-4-vinylcyclohexane and 1-isopropenyl-3-vinylcyclopentane;

aromatic polyenes, such as

divinylbenzene and vinylisopropenylbenzene.

These nonconjugated polyenes may be used in combination of two or more kinds.

Of these, nonconjugated polyenes having 7 or more carbon atoms, e.g., 7-methyl-1,6-octadiene (MOD), 5-ethylidene-2-norbornene (ENB) and dicyclopentadiene (DCPD), are preferably used in the invention.

(i) Ratio of (a) ethylene component to (b) α -olefin component [(a)/(b)]

The ethylene- α -olefin-nonconjugated polyene random copolymer provided by the invention contains units derived from ethylene (a) and units derived from the α -olefin of 3 or more carbon atoms (b) (sometimes referred to simply as " α -olefin (b)" hereinafter) in a molar ratio of 40/60 to 95/5 [(a)/(b)], preferably 55/45 to 90/10.

When this random copolymer is used as a blend with a conjugated diene rubber, the molar ratio (a)/(b) is preferably in the range of 65/35 to 80/20. From the random copolymer of this ratio and the conjugated diene rubber, a rubber composition having high mechanical strength and capable of exhibiting characteristics of rubbers even at low temperatures can be obtained.

(ii) Iodine value

The iodine value of the ethylene- α -olefin-nonconjugated polyene random copolymer, that is one index of the amount of the nonconjugated polyene component, is in the range of 1 to 50, preferably 5 to 40.

(iii) Intrinsic viscosity (η)

The intrinsic viscosity (η) of the ethylene- α -olefin-nonconjugated polyene random copolymer, as measured in decalin at 135 °C, is in the range of 0.1 to 8.0 dl/g, preferably 0.2 dl/g to 6 dl/g.

When this random copolymer is used as a blend with a conjugated diene rubber, the intrinsic viscosity (η) is particularly preferably 0.3 dl/g to 5 dl/g. The random copolymer having an intrinsic viscosity (η) of this range is excellent in blending properties (compatibility) with the conjugated diene rubber, and from the random copolymer and the conjugated diene rubber, a vulcanizable rubber composition excellent in not only mechanical strength but also heat resistance and weathering resistance can be obtained.

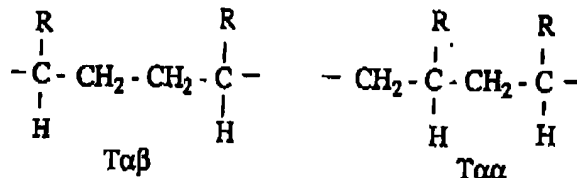
(iv) $T_{\alpha\beta}/T_{\alpha\alpha}$

The intensity (area) ratio D of $T_{\alpha\beta}$ to $T_{\alpha\alpha}$ of the ethylene- α -olefin-nonconjugated polyene random copolymer in the ^{13}C -NMR spectrum, $T_{\alpha\beta}/T_{\alpha\alpha}$, is not more than 0.5. The intensity ratio D of the random copolymer varies depending on

EP 0 718 325 A2

the kind of the α -olefin (b) for constituting the random copolymer, but it is preferably not more than 0.1, more preferably not more than 0.05.

$T_{\alpha\beta}$ and $T_{\alpha\alpha}$ in the ^{13}C -NMR spectrum are each a peak intensity of CH_2 in the units derived from the α -olefin of 3 or more carbon atoms (b), and they mean two kinds of CH_2 different in the position to the tertiary carbon as shown below.



The intensity ratio D of the random copolymer can be determined in the following manner.

The ^{13}C -NMR spectrum of the random copolymer is measured using a hexachlorobutadiene/ d_6 -benzene (2/1 by volume) mixed solution of a sample (concentration: 5 % by weight) at 25 °C and 67.8 MHz on the basis of d_6 -benzene (128 ppm) by means of a NMR measuring device (e.g., JEOL-GX270 produced by Japan Electron Optics Laboratory Co., Ltd.).

The ^{13}C -NMR spectrum thus measured was analyzed basically in accordance with the proposals of Lindemann Adams (Analysis Chemistry 43, p 1,245 (1971)) and J.C. Randall (Review Macromolecular Chemistry Physics, C29, 201 (1989)).

The intensity ratio D is now described in more detail with reference to an ethylene-1-butene-7-methyl-1,6-octadiene random copolymer.

In the ^{13}C -NMR spectrum of the ethylene-1-butene-7-methyl-1,6-octadiene random copolymer, the peak which appears at 39 to 40 ppm is assigned to $T_{\alpha\alpha}$, and the peak which appears at 31 to 32 ppm is assigned to $T_{\alpha\beta}$.

The intensity ratio D is calculated as a ratio between the integrated values of those peak areas.

The intensity ratio D thus obtained is considered an index of a proportion of occurrence of the 2,1-insertion reaction of 1-butene after the 1,2-insertion reaction or an index of a proportion of occurrence of the 1,2-insertion reaction after the 2,1-insertion reaction. Therefore, as the intensity ratio D becomes larger, the linkage direction of the α -olefin (1-butene) becomes more irregular. To the contrary, as the D value becomes smaller, the linkage direction of the α -olefin (1-butene) becomes more regular. When the regularity is high, the molecular chains tend to be assembled and the random copolymer tends to have high strength, and preferred in the present invention.

In the present invention, a random copolymer having the intensity ratio D of not more than 0.5 is obtained by copolymerizing ethylene, an α -olefin of 3 or more carbon atoms and a nonconjugated polyene using a catalyst containing a Group IVB metallocene compound, as described later. However, even if ethylene, 1-butene and 7-methyl-1,6-octadiene are copolymerized in the presence of a Group VB metallocene (e.g., vanadium) catalyst, an ethylene-1-butene-7-methyl-1,6-octadiene copolymer having the intensity ratio D of not more than 0.5 cannot be obtained. The same applies to other α -olefins than 1-butene.

(v) B value

The B value of the ethylene- α -olefin-nonconjugated polyene random copolymer, as determined by the ^{13}C -NMR spectrum and the following formula, is in the range of 1.00 to 1.50, preferably 1.02 to 1.50, more preferably 1.02 to 1.45, particularly preferably 1.02 to 1.40.

$$B \text{ value} = [P_{OE}]/(2 \cdot [P_E] \cdot [P_O])$$

wherein $[P_E]$ is a molar fraction of the units derived from ethylene (a) in the random copolymer, $[P_O]$ is a molar fraction of the units derived from the α -olefin (b) in the random copolymer, and $[P_{OE}]$ is a proportion of the number of the α -olefin-ethylene sequences to the number of all the dyad sequences in the random copolymer.

This B value is an index of a distribution state of the ethylene (a) and the α -olefin (b) in the random copolymer, and it can be determined based on the reports by J.C. Randall (Macromolecules, 15, 353 (1982)) and J. Ray (Macromolecules, 10, 773 (1977)).

As the B value becomes larger, the block-like sequence of the ethylene (a) or the α -olefin (b) becomes shorter, and this means that the sequence distribution of ethylene and the α -olefin is uniform and the composition distribution of the random copolymer is narrow. As the B value becomes smaller (particularly smaller than 1), the composition distribution

EP 0 751 182 A1

the copolymer rubber tends to be lowered.

(2) Iodine value

- 5 The iodine value of the ethylene/ α -olefin/nonconjugated polyene copolymer rubber (B1), that is one index of the amount of the nonconjugated polyene component in the copolymer rubber (B1), is in the range of 1 to 50, preferably 1 to 30.

(3) Intrinsic viscosity (η)

- 10 The intrinsic viscosity (η) of the ethylene/ α -olefin/nonconjugated polyene copolymer rubber (B1), as measured in decalin at 135 °C, is in the range of 0.1 to 10 dl/g, preferably 1.5 to 7 dl/g.

(4) $g\eta^*$ value

- 15 The $g\eta^*$ value determined by the intrinsic viscosity (η) of the linear ethylene/ α -olefin/nonconjugated polyene copolymer rubber (B1) exceeds 0.95.

The $g\eta^*$ value is defined by the following equation:

$$20 \quad g\eta^* = (\eta)/(\eta)_{\text{blank}}$$

- wherein (η) is an intrinsic viscosity measured in the property (3), and (η)_{blank} is an intrinsic viscosity of a linear ethylene/propylene copolymer which has the same weight-average molecular weight (measured by a light scattering method) as the copolymer rubber (B1) and has an ethylene content of 70 % by mol.

From the linear ethylene/ α -olefin/nonconjugated polyene copolymer rubber (B1) having such properties as mentioned above, a thermoplastic elastomer composition and a molded product thereof both of which are excellent not only in mechanical strength, weathering resistance and ozone resistance but also in low-temperature resistance (low-temperature flexibility) and heat resistance can be obtained.

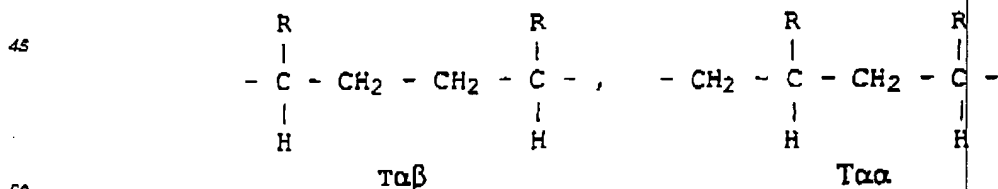
- 30 It is preferable that the linear ethylene/ α -olefin/nonconjugated polyene copolymer rubber (B1) further has the following properties (5) to (7).

(5) D value

- 35 The intensity (area) ratio D of $T\alpha\beta$ to $T\alpha\alpha$ in the ^{13}C -NMR spectrum of the ethylene/ α -olefin/nonconjugated polyene copolymer rubber (B1) $T\alpha\beta/T\alpha\alpha$, is not more than 0.5, preferably not more than 0.3.

The intensity ratio D of the copolymer rubber (B1) varies depending on the kind of the α -olefin used for forming the copolymer rubber (B1).

- 40 $T\alpha\beta$ and $T\alpha\alpha$ in the ^{13}C -NMR spectrum are each a peak intensity of CH_2 in the units derived from the α -olefin, and each respectively represents either of two kinds of CH_2 having different positions to the tertiary carbon as shown below.



The intensity ratio D of the copolymer rubber can be determined in the following manner.

- 55 The ^{13}C -NMR spectrum of the copolymer rubber is obtained by measuring a mixture solution of hexachlorobutadiene with a sample (concentration: 5 % by weight)/ d_6 -benzene (2/1 by volume) by means of a NMR measuring device (e.g., JEOL-GX270 manufactured by Japan Electron Optics Laboratory Co., Ltd.) at 25 °C and 67.8 MHz on the basis of d_6 -benzene (128 ppm).

Analysis of the ^{13}C -NMR spectrum was basically carried out in accordance with the proposals of Lindemann Adams (Analysis Chemistry 43, p1245 (1971)) and J.C. Randall (Review Macromolecular Chemistry Physics, C29, 201 (1989))

EP 0 751 182 A1

The intensity ratio D is now described in more detail with reference to an ethylene/1-butene/7-methyl-1,6-octadiene copolymer rubber.

In the ^{13}C -NMR spectrum of the ethylene/1-butene/7-methyl-1,6-octadiene copolymer rubber, the peak appearing at 39 to 40 ppm is assigned to $\text{T}\alpha\alpha$, and the peak appearing at 31 to 32 ppm is assigned to $\text{T}\alpha\beta$.

5 The intensity ratio D is calculated as a ratio between the integrated values of those peak areas.

The intensity ratio D thus determined is considered as an index of a proportion of occurrence of the 2,1-addition reaction of 1-butene subsequent to the 1,2-addition reaction or an index of a proportion of occurrence of the 1,2-addition reaction subsequent to the 2,1-addition reaction. Therefore, the larger the intensity ratio D becomes, the more irregular the linkage direction of the α -olefin (1-butene) becomes. To the contrary, the smaller the D value becomes, the more regular the linkage direction of the α -olefin (1-butene) becomes. When the regularity is high, the molecular chains tend to be assembled and the copolymer rubber tends to have high strength and is preferred.

10 In the present invention, a copolymer rubber (B1) having an intensity ratio D of not more than 0.5 is obtained by copolymerizing ethylene, an α -olefin and a nonconjugated polyene using a specific Group IVB metallocene catalyst as described later. However, even if ethylene, 1-butene and 7-methyl-1,6-octadiene are copolymerized in the presence of a Group VB metallocene (e.g., vanadium) catalyst, an ethylene/1-butene/7-methyl-1,6-octadiene copolymer rubber having an intensity ratio D of not more than 0.5 cannot be obtained. The same applies to other α -olefins than 1-butene.

(6) B value

20 The B value of the ethylene/ α -olefin/nonconjugated polyene copolymer rubber (B1), as determined by the ^{13}C -NMR spectrum and the following equation, is in the range of 1.00 to 1.50.

$$\text{B value} = (P_{OE}) / (2 \cdot (P_E) \cdot (P_O))$$

25

wherein (P_E) is a molar fraction of the ethylene units (a) in the copolymer rubber; (P_O) is a molar fraction of the α -olefin units (b) in the copolymer rubber; and (P_{OE}) is a proportion of a number of the α -olefin/ethylene sequences to a number of all the dyad sequences in the copolymer rubber.

This B value is an index of distribution of the ethylene and the α -olefin in the copolymer rubber, and it can be determined based on the reports by J.C. Randall (Macromolecules, 15, 353 (1982)) and J. Ray (Macromolecules, 10, 773 (1977)).

30 The larger the B value becomes, the shorter the block-like sequence of the ethylene or the α -olefin becomes, and this shows that the sequence distribution of the ethylene and the α -olefin is uniform and the composition distribution of the copolymer rubber is narrow. The smaller the B value becomes (particularly smaller than 1.00), the composition distribution of the copolymer rubber is widened, and such copolymer rubber does not sufficiently exhibit its properties such as strength when vulcanized, differently from a copolymer rubber of narrow composition distribution.

35 In the present invention, a copolymer rubber (B1) having a B value of 1.00 to 1.50 is obtained by copolymerizing ethylene, an α -olefin and a nonconjugated polyene using a specific Group IVB metallocene catalyst as described later. However, even if ethylene, an α -olefin and a nonconjugated polyene are copolymerized in the presence of a non-metallocene type titanium catalyst, an ethylene/ α -olefin/nonconjugated polyene copolymer rubber having a B value within the above range cannot be obtained.

(7) Glass transition temperature

45 The glass transition temperature (T_g) of the ethylene/ α -olefin/nonconjugated polyene copolymer rubber (B1), as measured by DSC (differential scanning calorimeter), is preferably not higher than -50°C .

From the copolymer rubber (B1) having a glass transition temperature (T_g) of not higher than -50°C , a thermoplastic elastomer composition of good low-temperature flexibility can be obtained.

50 The ethylene/ α -olefin/nonconjugated polyene copolymer rubber (B1) used in the invention, e.g., a random copolymer rubber of ethylene, 1-butene and ethylidene norbornene (ENB), has a glass transition temperature (T_g) lower by about 5 to 10°C than that of an ethylene/propylene/ENB random copolymer rubber (EPDM) having the same monomer ratio among ethylene, α -olefin and polyene as this copolymer rubber, and this copolymer rubber exhibits excellent low-temperature properties.

55 Properties of long-chain branched ethylene/ α -olefin/nonconjugated polyene copolymer rubber (B2)

The long-chain branched ethylene/ α -olefin/nonconjugated polyene copolymer rubber (B2) preferably used in the invention has the following properties.

BEST AVAILABLE COPY